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Exciplex Emission in Heterojunctions of Poly (pyridyl vinylene
phenylene vinylene)s and Poly (vinyl carbazole)

by

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Prepared for Publication in

Synthetic Metals

The Ohio State University
Department of Physics
Columbus, OH

DTIC QUALITY INSPECTED 2

September 20, 1997

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 9/20/97	3. REPORT TYPE AND DATES COVERED Technical

4. TITLE AND SUBTITLE
Exciplex Emissions in Heterojunctions of poly (pyridyl vinylene phenylene vinylene)s and poly (vinyl carbazole)

5. FUNDING NUMBERS
N00014-95-1-0302   and   N00014-92-J-1369

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAMES AND ADDRESS(ES)
Department of Physics
The Ohio State University
174 West 18th Avenue
Columbus, OH 43210-1106

8. PERFORMING ORGANIZATION REPORT NUMBER
P291

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Prepared for publication in Synthetic Metals

12a. DISTRIBUTION/AVAILABILITY STATEMENT
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12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

We present photoluminescence and electroluminescence spectra of heterojunctions formed from poly (vinyl carbazole) (PVK) and poly (pyridyl vinylene phenylene vinylene) (PPyVPV). Bilayers of PVK and PPyVPV show a photoluminescence peak which cannot be assigned to either the PVK or the PPyVPV layer. Absorption spectra show that the additional feature results from an exciplex at the bilayer interface. The electroluminescence spectrum from the heterojunctions is due to exciplex emission, with internal efficiencies of ~0.1-0.5%.

14. SUBJECT TERMS
Light-Emitting Devices, Electroluminescence, Photoluminescence, Heterojunctions, Poly (phenylene vinylene) and derivatives

15. NUMBER OF PAGES
4

16. PRICE CODE

17. SECURITY CLASS. OF RPT Unclassified	18. SECURITY CLASS OF THIS PG. Unclassified	19. SECURITY CLASS OF ABSTRCT. Unclassified	20. LIMITATION OF ABSTRACT Unlimited

Exciplex emission in heterojunctions of poly(pyridyl vinylene phenylene vinylene)s and poly(vinyl carbazole)

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Abstract

We present photoluminescence and electroluminescence spectra of heterojunctions formed from poly(vinyl carbazole) (PVK) and poly(pyridyl vinylene phenylene vinylene) (PPyVPV). Bilayers of PVK and PPyVPV show a photoluminescence peak which cannot be assigned to either the PVK or the PPyVPV layer. Absorption spectra show that the additional feature results from an exciplex at the bilayer interface. The electroluminescence spectrum from the heterojunctions is due to exciplex emission, with internal efficiencies of ~ 0.1-0.5%.

Keywords: Light-emitting devices, Electroluminescence, Photoluminescence, Heterojunctions, Poly(phenylene vinylene) and derivatives

1. Introduction

Conjugated polymer based light-emitting devices have become an extensive area of academic and industrial research since the report of electroluminescence (EL) in poly(phenylene vinylene) (PPV) in 1990 [1]. A great number of different conjugated polymers have been found to exhibit EL including PPVs [1-3], poly(phenylphenylene vinylene) [4], polyphenylenes [5-7], polythiophenes [8-9], polyquinolines [10], polypyridines [11-12], poly(pyridyl vinylenes) [12-14] and many copolymers of these materials. In addition to many different materials, numerous configurations have been used to change and improve device performance. For instance, the use of additional layers to improve device efficiency has been known for some time [2,15]. Inserting a hole-transport (electron blocking) layer between the anode and emitting polymer or an electron-transport (hole-blocking) layer between the cathode and emitting polymer can greatly improve efficiency by confining the majority carrier to the emitting layer. A well known hole-transport (electron blocking) layer is poly(vinyl carbazole) (PVK) which has a large band gap •(3.5 eV) and is itself luminescent [16-18].

We present results for bilayer devices using PVK as a hole-transport layer and a family of copolymers of PPV and poly(pyridyl vinylene) PPyV with various side groups as the emitting layers. The absorption, photoluminescence and electroluminescence spectra indicate that the PL and EL are attributed to the formation of an exciplex at the PVK/copolymer interface for all the copolymer systems studied. An exciplex, like an excimer, is an excited state complex, except that an exciplex is formed between two different molecules (polymers in this case) rather than identical ones for an excimer [19]. Contrary to expectations, earlier reported devices do not exhibit exciplex formation. For example, Greenham et al reported a bilayer device with CN-PPV and PPV, but the EL matches the PL and EL of a single CN-PPV film [3]. Results for other bilayer configurations also do not support exciplex formation [2].

Osaheni and Jenekhe [20] have observed exciplex formation in bilayers of PBO and TTA, but only for PL, although they do suggest that exciplexes may be important processes in organic light-emitting devices [20-21]. PL and EL due to exciplex formation has been reported in blends of PVK and a multiblock copolymer by Karasz and coworkers [17], but devices with separate layers were not investigated.
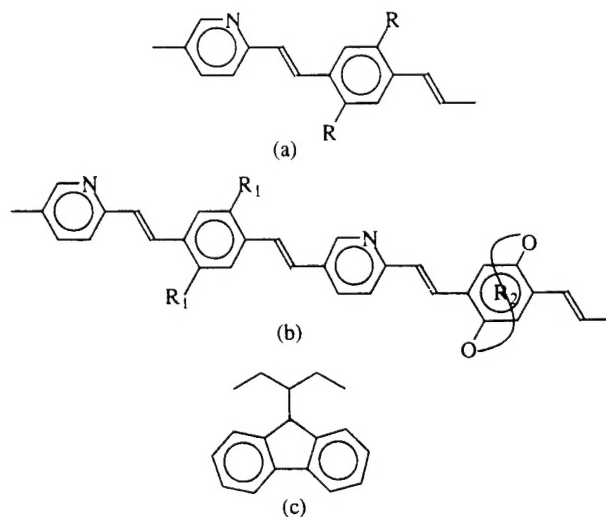

Fig. 1. (a) Copolymer of PPyV and PPV with side groups $R=C_{12}H_{25}$ or $COOC_{12}H_{25}$. (b) Copolymer with side group $R_1=OC_{16}H_{33}$ and strap $R_2=C_{10}H_{20}$. (c) Hole-transport layer poly(vinyl carbazole).

2. Experiment

The synthesis of the PPyVPV copolymers is described elsewhere [22]. Figure 1a shows the molecular structure of poly(pyridyl vinylene phenylene vinylene) (PPyVPV). We report results for copolymers with side groups $R=COOC_{12}H_{25}$ and $C_{12}H_{25}$. Figure 1b shows the same copolymer with a "strap" across the phenyl ring in alternate PPV segments. For the second copolymer the side groups are $R_1=OC_{16}H_{33}$ with a strap $R_2=C_{10}H_{22}$. The copolymers are soluble in common organic solvents such as tetrahydrofuran (THF), xylene, and chloroform. The PVK (Fig. 1c) was purchased from Aldrich Chemical Co. The PL and EL measurements were made using a PTI QM1 luminescence spectrometer. The absorption measurements were made using a Perkin Elmer Lambda 19 UV/Vis/NIR spectrometer. The current-voltage characteristics were measured using two Keithley 195A multimeters. The voltage was applied using a HP 6218A dc power supply. Quantum efficiency measurements were made using a calibrated QTH lamp and a United Detector Technologies Silicon Photodiode (UV-100).

The samples for PL and absorption measurements were spin cast on quartz. PVK was spin cast (~3000 rpms) from a 10 mg/ml solution in THF. The copolymers were all spin cast (~1000 rpms) from xylene (~ 10 mg/ml) so the underlying PVK layer was not dissolved. For devices the polymers were spin cast on indium tin-oxide (ITO) substrates, which had previously been cleaned. The PVK layer in the bilayer configurations was dried for ~ 30 seconds in a laminar flow hood before the copolymer layer was spin cast. All fabrication steps for the devices were conducted in an ambient atmosphere in a Class 100 cleanroom. Aluminum electrodes were thermally evaporated onto the copolymer surface at low pressures ($< 10^{-6}$ torr). The active area of the devices was 7 mm^2.

3. Results and Discussion

Figure 2 shows the absorbance for single and bilayer systems. Each of the plots shows the absorbance of a single layer of PVK, a single layer of a copolymer, and a bilayer configuration of PVK and the corresponding copolymer. The onset of PVK absorption is at 3.5 eV and shows two spectral features at 3.6 and 3.75 eV similar to previous reports [6,7]. In each of the three cases (a), (b) and (c) of Fig. 2 the absorbance of the bilayer configuration is the sum of the absorbance of each of the individual layers. No new ground to excited state transitions are present. Photoluminescence excitation (PLE) results (not shown) for each of the systems confirm these results.

The photoluminescence for the single layer and bilayer configurations are shown in Fig. 3. The PL (excited at 3.6 eV) of a PVK film is shown in Fig. 3a, 3b and 3c by the open circles (O) and peaks at 3.05 eV similar to previous reports [6,7]. The dashed line is the PL of a single layer film of each copolymer, (a) PPyVP(C$_{12}$H$_{25}$)$_2$V, (b) PPyVP(COOC$_{12}$H$_{25}$)$_2$V and (c) the strapped copolymer. The spectra are similar with each of the peaks at ~ 2.1 eV with the exception of the strapped copolymer which also has a significant shoulder at 2.25 eV. The PL of the copolymer films, which peak near 2.6 eV [23], are significantly redshifted from that of the solution PL (not shown). The PL
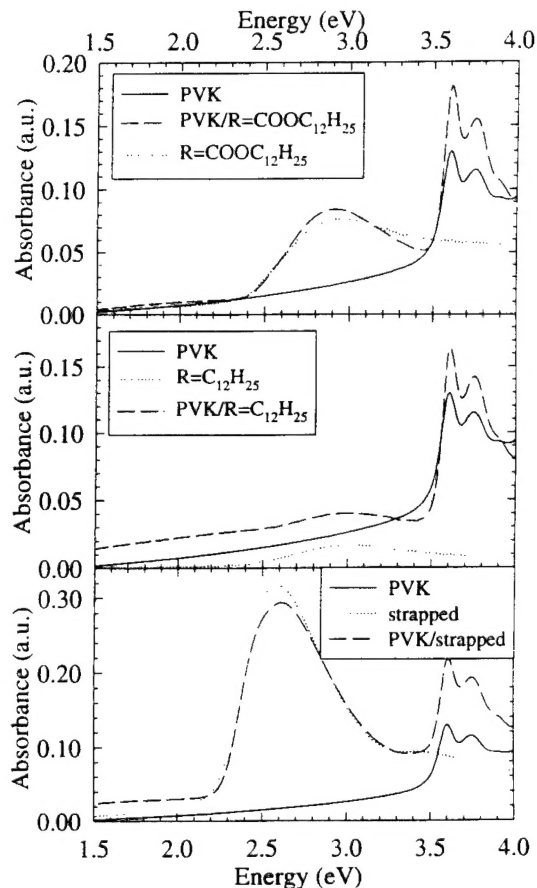

Fig. 2. Absorbance of a single layer of PVK, a single layer of copolymer, and a bilayer of PVK/copolymer. (a) PPyVP(COOC$_{12}$H$_{25}$)$_2$V, (b) PPyVP(C$_{12}$H$_{25}$)$_2$V and (c) strapped copolymer.

redshift from solution to film is due to aggregation in the copolymer films [23].

The solid lines in Fig. 3 are the PL spectra for the bilayer configurations of PVK and each of the copolymers. In each case the bilayer films were excited at 3.6 eV an energy that is greater than the band gap of PVK. In each case, more prominently in Figs. 3b and 3c, there is PL emission at the same energy as the PVK PL emission (3.1 eV). However, the main feature in the PL of the bilayer films is located at 2.5 eV for (a) PPyVP(C$_{12}$H$_{25}$)$_2$V and (b) PPyVP(COOC$_{12}$H$_{25}$)$_2$V and at 2.4 eV for the (c) strapped copolymer. Emission at these energies is not observed for individual films of either PVK or the copolymers indicating that the emission is due to a completely different species, the exciplex. When the excitation energy is lowered below 3.4 eV (band gap of PVK) the emission due to the exciplex is drastically reduced. In addition, varying the concentration or thickness of the copolymer or PVK films in the bilayer configuration will change the relative strengths of the exciplex peak and PVK peak.
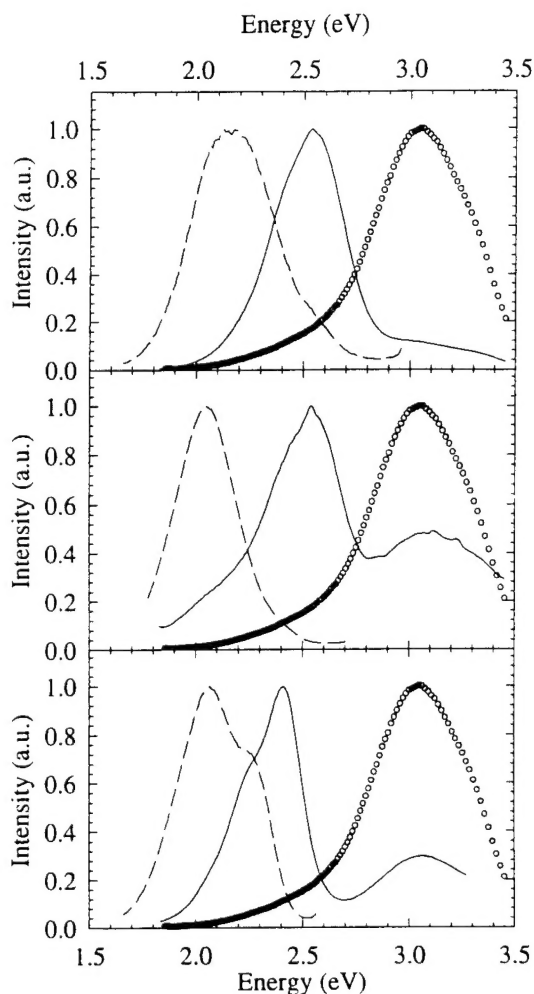
Fig. 4. Electroluminescence (solid lines) for a (a) ITO/PVK/ PPyVP(COOC$_{12}$H$_{25}$)$_2$V/Al device and a (b) ITO/PVK/strapped copolymer/Al device. Photoluminescence (dashed lines) for bilayer films of PVK and (a) PPyVP(COOC$_{12}$H$_{25}$)$_2$V and (b) strapped copolymer.

Fig. 3. Photoluminescence of (a) PPyVP(C$_{12}$H$_{25}$)$_2$V film (dashed line), PVK/PPyVP(C$_{12}$H$_{25}$)$_2$V bilayer film (solid line), PVK film (O) (b) PPyVP(COOC$_{12}$H$_{25}$)$_2$V film (dashed line), PVK/ PPyVP(COOC$_{12}$H$_{25}$)$_2$V bilayer film (solid line), PVK film (O), and (c) strapped copolymer.film (dashed line), PVK/strapped copolymer bilayer film (solid line), PVK film (O).

PPyVP(C$_{12}$H$_{25}$)$_2$V and PPyVP(COOC$_{12}$H$_{25}$)$_2$V have nearly identical PL results, which is expected since the side chains tend to perform the same function in both copolymers. The single layer PL results for the strapped copolymer in Fig. 3c show a completely new feature, a high energy shoulder. The high energy shoulder is closer to the solution PL and is attributed to unaggregated sites in the film. The C$_{10}$H$_{20}$ strap around every other phenyl ring tends to disturb the aggregation that occurs in the other copolymers of this family. The same shoulder (now on the low energy side) also appears in the bilayer film, indicating the PL has contributions from exciplex sites and from unaggregated regions of the strapped copolymer.

We have fabricated single and bilayer devices using ITO as the anode and aluminum as the cathode. Figures 4a and 4b show
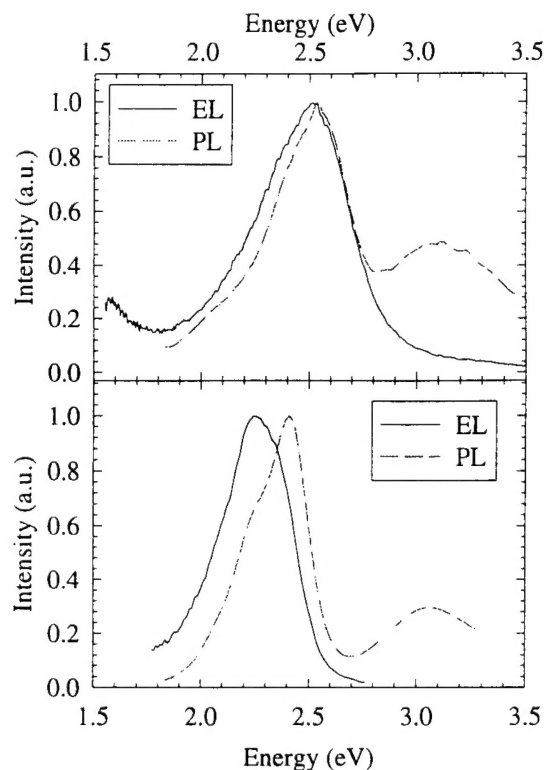
the EL of (a) ITO/PVK/PPyVP(COOC$_{12}$H$_{25}$)$_2$V/Al device and (b) ITO/PVK/strapped copolymer/Al device. For comparison the PL of the equivalent bilayer films from Fig. 3 are shown. Figure 4a shows excellent agreement between the EL and PL for the bilayer device and bilayer film for PPyVP(COOC$_{12}$H$_{25}$)$_2$V, which indicates the EL is from the same species, the exciplex, as the PL. The EL for the bilayer, strapped copolymer device (Fig. 4b) is red-shifted somewhat from the PL of the bilayer film. The EL appears to agree with the low energy shoulder present in the PL of the bilayer film (Figs. 4b and 3c) and with the high energy shoulder present in the PL of the single layer film (Fig. 3c). This EL emission, peaked at 2.25 eV is in between the PL of the single layer film and bilayer film and indicates the EL is a combination of exciplex emission and emission from unaggregated sites in the strapped copolymer.

The bilayer devices have turn-on voltages ~ 12-16 volts with current densities between 0.1 and 0.5 mA/mm^2. The devices can easily be seen in a brightly lit room and have internal quantum efficiencies ~ 0.1-0.5%. Figure 5 shows the current-voltage (O) and voltage-brightness (solid line) characteristics for a typical ITO/PVK/PPyVP(COOC$_{12}$H$_{25}$)$_2$V/Al bilayer device. The inset of

Fig. 5 shows a comparison between a single layer device $(ITO/PPyVP(COOC_{12}H_{25})_2V/Al)$ and the bilayer device shown in the main plot. The bilayer device is ten times brighter at an order of magnitude lower current density which means the bilayer device is ~ 100 times more efficient than the single layer device.
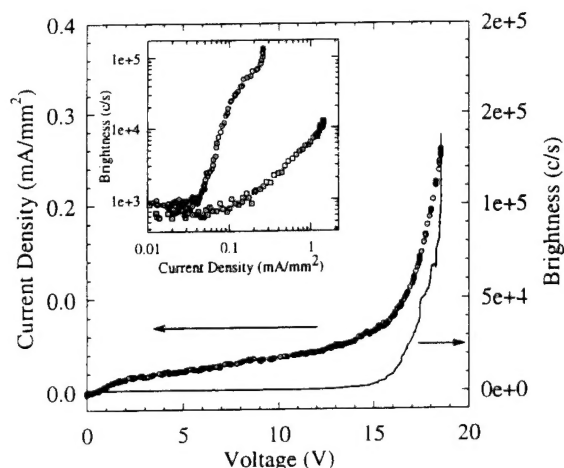

Fig. 5. Current density-voltage characteristics (O) and brightness-voltage characteristics of an $ITO/PVK/PPyVP(COOC_{12}H_{25})_2V/Al$ device. Inset shows a comparison between a single layer, $ITO/PPyVP(COOC_{12}H_{25})_2V/Al$, device ($\square$) and the bilayer device (O). The bilayer device is 10 times brighter at 10 times lower current density implying a 100 times improvement in efficiency.

In the devices the electrons are injected from the Al electrode into the conduction band of the copolymer, but they are confined at the PVK/copolymer interface due to a large barrier. The holes injected from the ITO also may be confined at the interface by a somewhat smaller barrier. The increased number of electrons and holes in the interface region increase the probability of recombination via exciplex emission. In addition the buried interface severely reduces the non-radiative recombination that otherwise will occur near the electrodes.

4. Conclusion

In summary, we have shown the presence of exciplex emission in heterojunctions of PVK and $PPyVP(R)_2V$. The addition of a $C_{10}H_{20}$ strap on every other phenyl ring in the copolymer reduces the aggregation in the films. Emission from the strapped copolymer bilayers is a combination of light from exciplex and unaggregated sites. The exciplex is the primary method of electroluminescence in the bilayer devices. The bilayer devices we have fabricated show a 100 times increase in efficiency compared to single layer devices due to charge confinement and exciplex emission at the interface.

5. Acknowledgments

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